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Homogeneous *cis*-dihydroxylation and epoxidation of olefins with high H₂O₂ efficiency by mixed manganese/activated carbonyl catalyst system

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Abstract—The use of [Mn₂O₃(tmtacn)₂](PF₆)₂ (tmtacn = 1,4,7-trimethyl-1,4,7-triazacyclononane) in combination with glyoxylic acid methylester methyl hemiacetal (GMHA) results in a highly active and hydrogen peroxide efficient catalyst for the epoxidation of olefins as well as the first homogeneous catalytic *cis*-dihydroxylation system with H₂O₂ and with turnover numbers up to 420. © 2002 Elsevier Science Ltd. All rights reserved.

For economic and environmental reasons catalytic olefin oxidations based on O₂ or H₂O₂ are preferred over traditional stoichiometric oxidations, e.g. epoxidation with peracids and *cis*-dihydroxylation with permanganate.¹ Several methods are available for catalytic epoxidation with aqueous H₂O₂ (notably Re-, W-, and Mn-based catalysts),² but high turnovers for *cis*-dihydroxylation are only achieved using Os.³ However, the high cost and toxicity of Os hamper large scale application and provide a strong incentive to develop benign Fe- or Mn-based *cis*-dihydroxylation catalysts. Que et al. recently reported the first *cis*-dihydroxylation with H₂O₂ catalysed by a non-heme iron complex.⁴ Although this system shows good *cis*-diol selectivities, turnover numbers (t.o.n.) are rather low (up until 22 t.o.n.).

Recently Mn complexes based on tmtacn were found to be highly active in catalytic oxidation,⁵ but apart from high turnover, it is essential to develop catalytic systems that employ H₂O₂ very efficiently, as many Mn or Fe

catalysts are known to be particularly effective in decomposition of H₂O₂.⁶ This can be suppressed by working in acetone;⁷ however, this solvent is not acceptable for large-scale applications because of the risk of formation of explosive cyclic peroxides. H₂O₂ decomposition by Mn–tacn complexes can be suppressed by addition of oxalate^{8a} or ascorbic acid^{8b} as co-catalysts, or by anchoring the tacn ligand to a solid support.⁹ Significant amounts of *cis*-diols besides epoxides are formed during alkene oxidation with this heterogeneous Mn catalyst.

Herein, we report efficient alkene oxidations with H₂O₂ catalysed by Mn–tmtacn **1**¹⁰ in the presence of GMHA **2** (Fig. 1). Surprisingly, the latter not only strongly suppresses H₂O₂ decomposition by the Mn catalyst, but also imparts the first homogeneous catalytic *cis*-dihydroxylation activity to a Mn catalyst. Catalytic oxidations were performed by adding aqueous, 50% hydrogen peroxide (1.3 equiv. with respect to the sub-

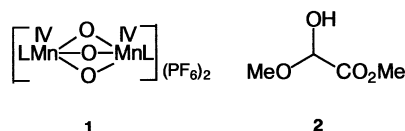


Figure 1. L = 1,4,7-trimethyl-1,4,7-triazacyclononane.

Keywords: hydrogen peroxide; *cis*-diols; epoxides; manganese; oxidation.

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strate) in 6 h to a mixture of alkene, Mn–tmtacn catalyst (0.1 mol%), and GMHA (25 mol%) in MeCN at 0°C. Under these reaction conditions, the presence of GMHA as the co-catalyst enables high conversions with only a 30% excess of oxidant with respect to substrate (Table 1) and the H₂O₂ efficiency is drastically improved compared to previous Mn systems using excess of H₂O₂.⁵ In most cases the conversions were also significantly higher than those obtained with oxalate as co-catalyst and 1.3 equiv. of H₂O₂ (for similar experiments with a larger excess of H₂O₂, see Ref. 8a).

In particular, styrene afforded a high yield of styrene oxide in the presence of GMHA, whereas the use of oxalate resulted in only modest conversion of styrene. When a mixture of GMHA (25 mol%) and oxalate (0.3 mol%) was used as the co-catalyst system, the epoxide yields even surpassed those obtained with the Mn/GMHA catalytic system, and high epoxide yields at complete conversion were obtained for the non-sterically hindered alkenes (Table 1, entries 1–3, 6, 8). Unexpectedly, substantial amounts of *cis*-diols were formed besides epoxides when *only* GMHA was present as the co-catalyst. The epoxide/*cis*-diol ratio depends

strongly on the alkene structure. The highest amount of *cis*-diol was found for cyclooctene (entry 3), which afforded the *cis*-diol as the main product (42%, 420 t.o.n.) besides the epoxide (36%, 360 t.o.n.). Minor amounts of 2-hydroxycyclooctanone were also found due to overoxidation of the diol. The ring size of cycloalkenes has a profound influence on the epoxide/*cis*-diol ratio (entries 1–4). For these cyclic olefins, almost no *trans*-diol could be detected (ratio *cis*-diol/*trans*-diol >99.5/0.5). *cis*-Diol formation is also observed for aliphatic acyclic alkenes. Yields of diol are significantly lower for *trans*-2-hexene than from *cis*-2-hexene, but the epoxide/*cis*-diol ratio was similar for both substrates. The aryl-substituted alkenes (entries 7, 8) yield epoxide nearly exclusively under these conditions. Limited *cis/trans* isomerisation is observed in the epoxide formation of *cis*-2-hexene. The *cis/trans* isomerisation points to epoxidation via a Mn oxo species, with formation of epoxides from C-centred radical intermediates with a lifetime sufficient for some C–C bond rotation prior to reaction to the epoxide.¹² In line with this mechanism, olefins that form a relatively long-lived radical intermediate, such as *cis*-stilbene, show substantial loss of configuration in epoxide. No diols were formed on replacing the substrate by epox-

Table 1. Oxidation of selected olefins by H₂O₂ with catalyst 1¹¹

Entry	Substrate	Conversion (%) ^c			Product ^d	Turnover number (t.o.n.) ^c		
		Additive: GMHA ^a (2)	Additive: 2 + oxalate ^b	Additive: oxalate ^c		Additive: GMHA ^a (2)	Additive: 2 + oxalate ^b	Additive: oxalate ^c
1	Cyclopentene	97	100	92	Epoxide	610	860	770
					<i>cis</i> -Diol	260	0	0
					Cyclopentenone	80	10	100
2	Cyclohexene	88	100	73	Epoxide	590	820	610
					<i>cis</i> -Diol	90	0	0
					2-Cyclohexenone	80	80	70
3	Cyclooctene	90	100	52	Epoxide	360	840	410
					<i>cis</i> -Diol	420	60	0
					2-HO-cyclooctanone	220	80	0
4	Norbornylene	95	88	59	<i>exo</i> -Epoxide	540	530	360
					<i>exo-cis</i> -Diol	180	60	0
5	<i>trans</i> -2-Hexene	77	93	37	<i>trans</i> -Epoxide	210	550	240
					<i>cis</i> -Epoxide	50	30	0
					<i>RR/SS</i> -Diol	150	90	0
					<i>RS/SR</i> -Diol	0	0	0
					<i>cis</i> -Epoxide	450	820	640
6	<i>cis</i> -2-Hexene	93	100	80 ^f	<i>trans</i> -Epoxide	40	30	20
					<i>SR/RS</i> -Diol	280	10	10
					<i>RR/SS</i> -Diol	10	0	0
					<i>cis</i> -Epoxide	260	260	110
					<i>trans</i> -Epoxide	200	160	150
7	<i>cis</i> -Stilbene	82	77	32	<i>meso</i> -Hydrobenzoin	40	30	10
					Hydrobenzoin	40	20	10
					Epoxide	860	860	380
8	Styrene	97	100	44	Ph(CH)(OH)CH ₂ OH	60	50	0
					PhC(O)CH ₂ OH	10	30	0

^a Co-catalyst GMHA (25 mol%).

^b Co-catalyst mixture of GMHA (25 mol%) and oxalate (0.3 mol%).

^c Co-catalyst oxalate (0.3 mol%), for similar experiments with a larger excess of H₂O₂, see Ref. 8a.

^d All products were identical to independent samples and identified by GC and ¹H NMR.

^e Determined by GC.

^f 32 mmol scale

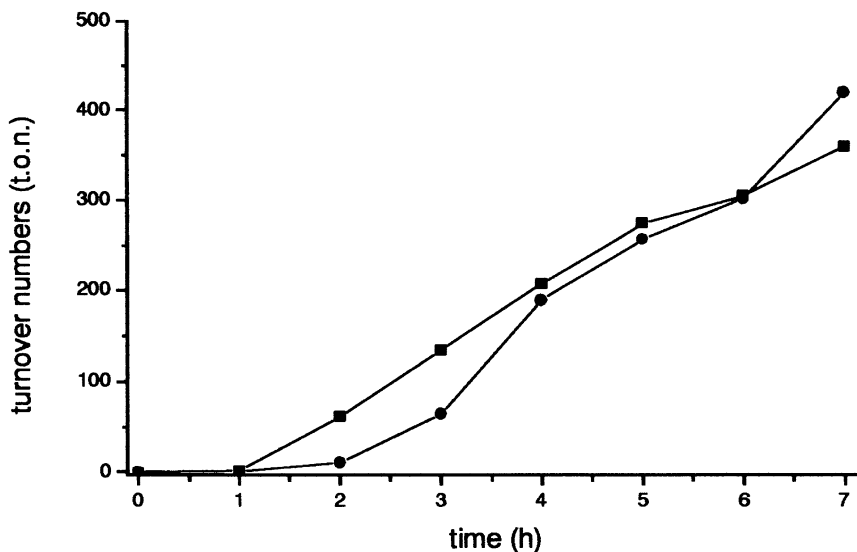
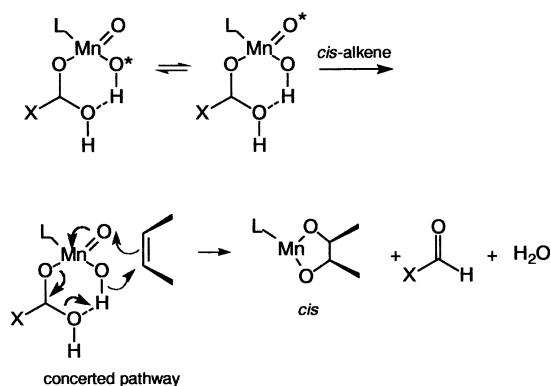


Figure 2. Time profile of the oxidation of cyclooctene by H_2O_2 with catalyst **1** and GMHA; ■ epoxide; ● *cis*-diol.

ide, thus excluding epoxide hydrolysis.¹³ This conclusion is further supported by the time course profile of the **1**/GMHA-catalysed oxidation of cyclooctene, which shows that both epoxide and diol increase progressively with time (Fig. 2).

Attempts to increase the *cis*-diol selectivity by addition of acid or base resulted in a dramatic decrease of conversion. Besides GMHA, a few other carbonyl compounds were tested as co-catalyst (25 mol%) for the oxidation of cyclooctene with H_2O_2 (1.3 equiv.). In the presence of glyoxylic acid hydrate, the epoxide was formed in 840 t.o.n. and *cis*-diol formation was almost completely suppressed. Modest *cis*-diol yields (<250 t.o.n.) and predominant formation of the epoxide were seen with diethyl ketomalonate or 2-ketoglutaric acid as the co-catalysts. However, *cis*-diol formation (370 t.o.n.) predominated over epoxide (310 t.o.n.) formation in the presence of chloral hydrate. Thus, a variety of carbonyl compounds with an adjacent electron withdrawing group are able to reduce H_2O_2 decomposition by **1** and to impose *cis*-dihydroxylation activity on manganese catalyst **1**, albeit with variable *cis*-diol/epoxide ratios.

Since *cis*-diol formation through Mn-catalysed epoxide hydrolysis can be excluded (vide supra), we propose that the *cis*-diol is formed by reaction of the alkene with an Mn oxo-hydroxo species. As in the case of oxalate, hydrated activated carbonyl compounds¹⁴ might break down the catalase active binuclear Mn complex **1**¹⁵ into a mononuclear Mn species via complexation to the Mn centre. *cis*-Diol formation from an Mn oxo-hydroxo species with a coordinated hydrated carbonyl ligand could be induced through a hydrogen bonded six-membered ring transition state (concerted pathway, Scheme 1). Reoxidation of the Mn centre with H_2O_2 , release of the diol from Mn, and hydration of the carbonyl compound closes the catalytic cycle. In conclusion, use of activated carbonyl compounds in



Scheme 1. Proposed *cis*-dihydroxylation mechanism (L = tmtacn, X = CO_2Me , CCl_3).

combination with Mn–tmtacn results in a highly active (up to 860 t.o.n.) and H_2O_2 efficient epoxidation system. Besides epoxidation this new catalytic system also provides, to the best of our knowledge, the most active Os-free homogeneous catalyst for *cis*-dihydroxylation (up to 420 t.o.n.). Compared with the anchored Mn–tmtacn catalyst,⁹ the present homogeneous **1**/activated carbonyl compound system is much more accessible, since both **1** and many activated carbonyl compounds have large scale applications. Efforts to enhance diol selectivity and to elucidate the *cis*-dihydroxylation mechanism are in progress.

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11. Typical oxidation procedure with Mn–tmtacn/GMHA system: H₂O₂ (50% aq., 52 mmol) was added in 6 h at 0°C to a solution of Mn₂O₃(tmtacn)₂(PF₆)₂ (**1**, 0.04 mmol), GMHA (10 mmol), substrate (40 mmol) and internal standard (1,2-dichlorobenzene, 20 mmol) in acetonitrile (40 mL). Samples for GC (HP 6890, column HP1 15×0.3 mm×2.65 μm, polymethylsiloxane) analysis were taken 1 h after complete addition of oxidant.
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